

Designing a Water-quality Monitor Using an Array of Ion Selective Electrodes¹

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Abstract—This effort is directed at developing a sensor for evaluating water quality. A set of nine ion selective electrodes (ISEs) are being fabricated on a 4.5-cm diameter ceramic substrate. The personalization of the ISEs uses a doping chamber that contains an electrolyte with a selected ionophore. A specific array element (electrode) is electronically selected and the desired ionic species is incorporated by electromigration and/or electropolymerization into the hydrogel layer. Subsequently, using a new solution, the specific ionophore is incorporated into a second polymer layer. This customization process is repeated for each of the other nine ion-specific elements of the array. This paper discusses the design and fabrication of the deposition chamber and the ceramic substrates that contain the ISEs.

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1. INTRODUCTION

This effort is based on an ion selective electrode (ISE) array developed for the MECA (Mars Environmental Compatibility Assessment) project [1]. In that effort 20 prefabricated ISEs were individually mounted into the walls of a 25-cm³ housing. The container was designed to be capable of analyzing the ionic content of Martian soils.

The target ions selected for this effort are K⁺ (340 mg/L), Ca²⁺ (30 mg/L), Mg²⁺ (50 mg/L) and Cl⁻ (200 mg/L) representing some of the NASA Spacecraft Maximum Contaminant Levels (MCL) for potable water for International Space Station Alpha. This is a joint effort between Tufts University, and Orion Research, Inc. who have many years of experience in the fabrication of ISE's and in water quality measurements and JPL which has experience in arraying sensors on ceramic substrates.

2. CERAMIC SUBSTRATE

The development of carrier-based polymeric membrane ISEs, whose key components are a lipophilic complexing agent (ionophore) capable of reversibly binding the analyte and a solvent polymeric membrane, has dramatically expanded the number of analytes amenable to potentiometric analysis. As seen in Figure 1 the membrane is composed of a high viscosity, water-immiscible "liquid." With one face exposed to the sample and the other to the internal reference electrode (electrolyte), it acts as the "transducer," converting a chemical concentration gradient into an electrical potential difference.

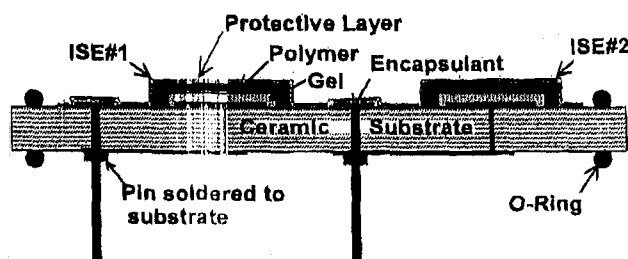


Fig. 1. ISE sensor array fabricated on a ceramic substrate.

The carrier based system relies on the ionophore to control transport and generate a gradient of the analyte through the membrane, while the ion-exchange system takes advantage of the exchange equilibrium between the analyte ion and an ionic exchanger. The selectivity of the membrane is a result of these ion exchange equilibria. The selectivity is related to the constants of the exchange equilibrium for the analyte and interfering ions at the organic/aqueous membrane interface, and strongly depends on the ratio of the complex formation constant to the ionophore in the membrane phase.

The ISE substrates, shown in Figure 1, are prepared using the same technology used to fabricate hybrid microelectronic circuits on co-fired ceramic substrates [2]. In our case the substrate is a 1-mm thick 96% alumina layer with an as-fired surface. Electrical connection is achieved via 0.5-mm diameter pins soldered to the underside of the ceramic. Conducting Pd-rich Ag layers are screen printed on the ceramic and fired in air at 840 °C. Conducting vias are formed by filling laser machined holes with Ag-Pd. The site of the pin is offset from the location of the ISEs. This was required to accommodate the conducting vias.

A photograph of the top side of the 4.5-cm diameter ceramic substrate is shown in Figure 2a. The ISEs are arrayed in a 3 × 3 matrix with working (WE) and reference (RE) electrodes. The WE is coated as indicated in Figure 1. The RE is basically uncoated. The thermometer, formed by screen printing RuO₂, is used to monitor the temperature of the electrolyte during deposition.

The bottom side of the ceramic substrate is shown in Figure 2b. The electrical pins are nickel-plated stainless steel attached to the underside of the ceramic with 60/40 Sn/Pb solder with an RMA flux. As seen in Figure 1, the pins penetrate only partly into the ceramic. The top of the hole occupied by the pin is sealed with an alumina filled SiO₂ dielectric encapsulant screened printed prior to insertion of the pins.

The ceramic substrates are placed in the deposition chamber. A water-tight seal is achieved via circular O-rings seen in Figure 1. As seen in the figure two O-rings are placed on the top and bottom of the ceramic so that the ceramic does not experience tensile stresses. Such stresses could crack the ceramic. Contact to the pins is accomplished using a ZIF (Zero-Insertion Force) socket to be shown later. This too minimizes the stress on the ceramic thus reducing the chance of cracking.

3. DEPOSITION CHAMBER

Once the high temperature processing steps are complete, the gel layer is deposited via screen printing. Then the substrate is placed in the deposition chamber and

ionophores are introduced in an aqueous solution. The ionophores are deposited on the gel of a particular cell by electronically addressing the cell. Once complete, the ionophore is removed and a new ionophore introduced and directed electronically to the next cell. This process is repeated until all the cells are addressed. Then the polymer layer is deposited and the process repeated.

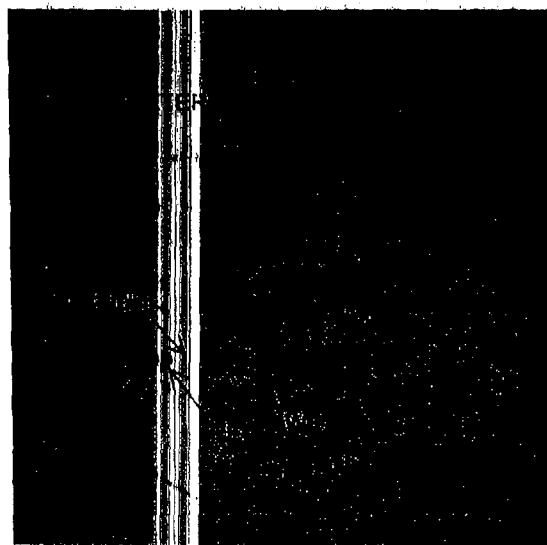


Fig. 2a. A 4.5-diameter ceramic substrate showing the working (WE) and reference (RE) electrodes arranged on a 3 × 3 array and a four-terminal thermometer.

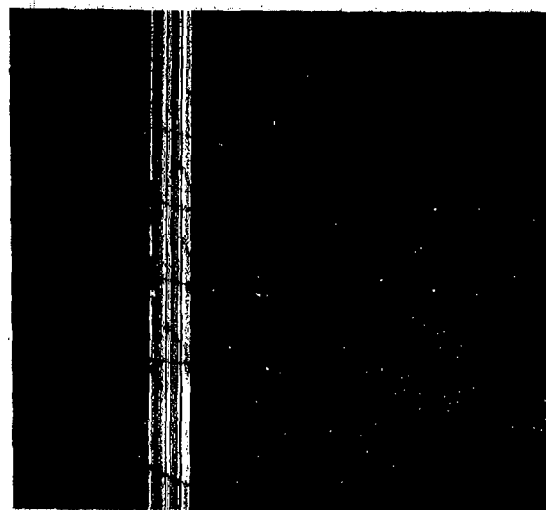


Fig. 2b. Ceramic substrate showing the pins that connect to the electrodes fabricated on the top side of the ceramic.

The three parts of the deposition chamber are shown in Figure 3. One of the O-rings is shown in the Base. The other sealing O-ring is located in the underside of the Clamp and is not shown. The under side of the Cap contains the counter electrode (CE) array. The top of the Cap contains the connections to the CE (not shown).

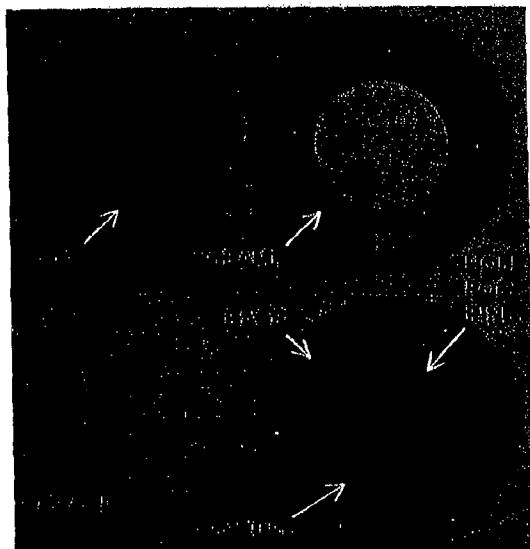


Fig. 3. Deposition chamber components including the ceramic substrate (lower left) and three chamber units: Base (lower right), Clamp (upper right), and Cap (upper left). The ceramic substrate is held in place by two O-rings: one O-ring is shown in the Base and the other O-ring is found on the underside of the Clamp.

4. DEPOSITION CHAMBER ELECTRONICS

Figure 4 shows the deposition chamber mounted on the electronics board. The deposition chamber is resting on the ZIF socket mentioned above. The cable is used to bring voltage to the counter electrodes mounted in the cap of the deposition chamber.

The circuitry, shown in Figure 5, allows for deposition at the addressed cell. That is, the ionophores in the electrolyte are directed to the selected WE. In the figure, the multiplexers are symbolized by the switches. Notice that each cell has four switches that are addressed via three digital lines.

The cells can be operated in either of two modes: potentiostatic or galvanostatic. In the potentiostatic mode a constant voltage is maintained between RE and WE. In the galvanostatic mode, a constant current is maintained through each cell by measuring the voltage drop across the resistor R0.

The main current flow is indicated for Cell #2 by the red (heavy) line. The current follows through two multiplexers

whose resistance is about 100 ohms each. Voltages for RE and WE are sensed at two other multiplexers. In this case the resistance of the multiplexers is inconsequential because the current drawn by the instrumentation amplifiers, IAs, is small. All of elements in the array that are not addressed are tied to CE through 1 Megaohm resistors to inhibit deposition except at the selected WE. The apparatus is designed with bipolar potentials so that either positively or negatively charged ionophores can be deposited.



Fig. 4. Deposition chamber mounted on the circuit board using a zero-insertion force (ZIF) socket.

5. RESISTOR CARD

In developing experimental equipment, it is important to develop as many checks as possible. This circuitry has at three checks points to help in problem solving. First, the pilot lamp indicates that the board is powered. Second, by placing a finger on the on-board thermometer (LM35), one can verify that the analog signals are being acquired by the data acquisition system and transmitted to the computer.

Third, the resistor card seen in Figure 6 is used to verify that the multiplexing addressing is correct. The resistor card is fabricated with an array of resistors that are different for each cell. When voltage is applied to the network, a unique voltage is produced for each cell and this is used to verify the correctness of the addressing circuitry and software.

6. ION SELECTIVE ELECTRODE

Figure 7 shows the typical responses obtained for polymer ISE for several ionic species in solutions that ranging from a 10^{-6} to 0 M of the respective ions. The Nernst response of the array, were obtained using ISEs from Orion Research, Inc. The slope depends on the sign and amount mount of ionization of each ion. This response represents a benchmark performance against which our ISE array must achieve.

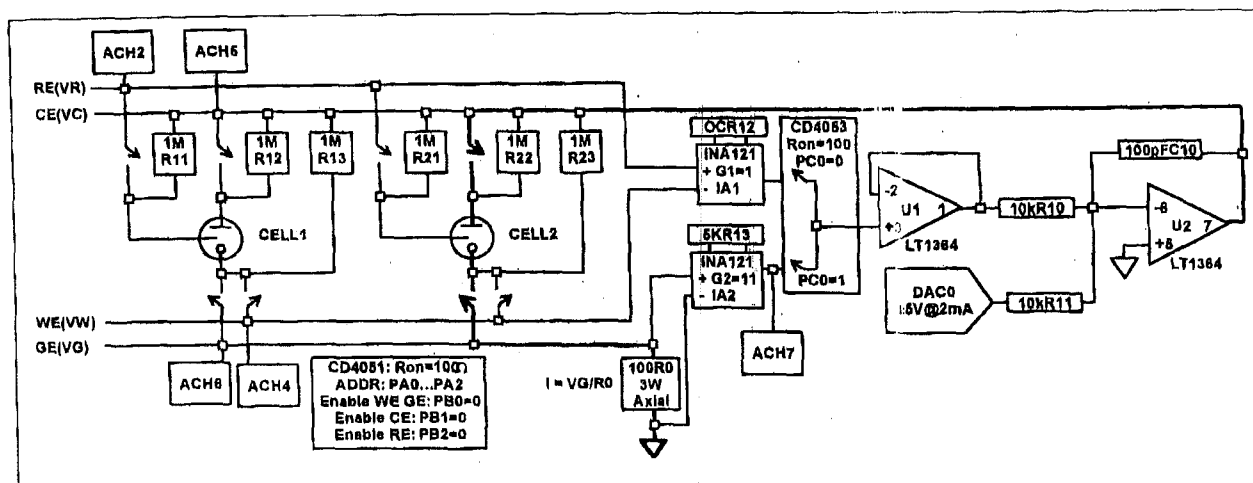


Fig. 5. Deposition Chamber Circuitry.

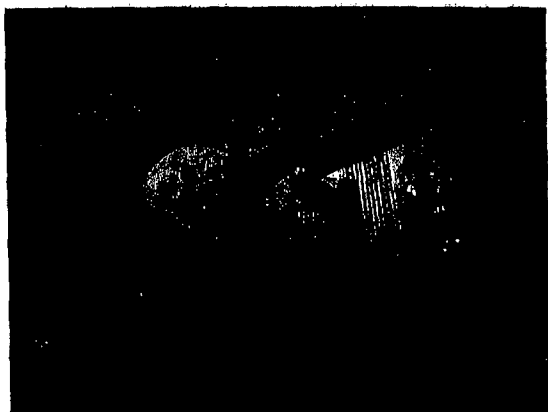


Fig. 6. Resistor card mounted on the deposition chamber circuit board.

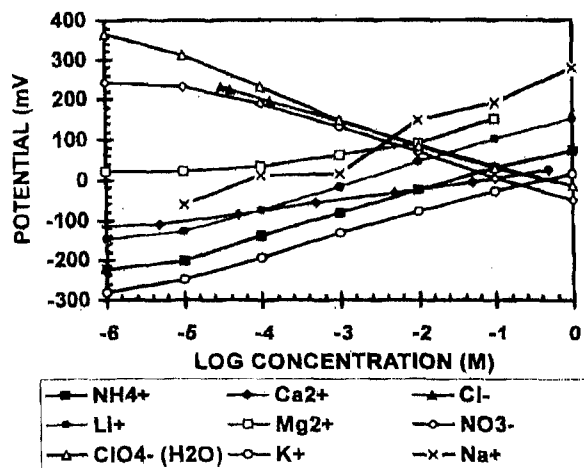


Fig. 7. ISE response from to several ions.

7. CONCLUSION

The development of an array of ISEs involves the selective doping of the array. In this new effort, the ISE's are personalized by electrically directing the ions in an aqueous solution to the selected cell. This paper describes the equipment needed to conduct this effort. In the coming months, detailed experiments will be performed to validate the approach and to characterize the detection sensitivities and the lifetime of the ISEs.

8. REFERENCES

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9. ACKNOWLEDGMENTS

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10. BIOGRAPHIES

Martin G. Buehler received the BSEE and MSEE from Duke University in 1961 and 1963, respectively and the Ph.D. in EE from Stanford University in 1966 specializing

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Samuel P. Kounaves received his BS/MS from Cal State - San Diego in 1976/78 and his Ph.D. (D.Sc.) from the University of Geneva in Switzerland in 1985. After a post-doctoral fellowships at SUNY-Buffalo and Harvard University he joined the faculty at Tufts University in 1988, where he is currently an Associate Professor of Chemistry. He has an active research group of 8 Ph.D. students and one undergraduate. He has been a principal investigator on more than 15 grants from government (NSF, EPA, DOE) and industry (PRF, EG&G, Orion). He has authored over 50 publications and holds 3 Patents. His research has been directed at the development of microfabricated electrochemical and chemically modified sensors; for use in monitoring and investigation of remote hostile environments, especially planetary bodies. Most

recently he has been involved with NASA's Jet Propulsion Laboratory to include several sensor arrays on the next Mars Lander for performing chemical analysis of the Martian soil.

Dennis P. Martin received his BSME from California State Polytechnic University in 1976 and pursued graduate work in Material Sciences of Microelectronics at Arizona State, California Institute of Technology, and University of Florida. Dennis joined the Jet Propulsion Laboratory and in 1981 formed Halcyon Microelectronics, Inc. As president of Halcyon Microelectronics, Dennis heads up the advanced packaging for research and development with emphasis on miniaturization of complex systems for hostile environments; i.e., high radiation, high "g" force, and extreme temperature. Halcyon offers a laboratory in which products are developed. More than 300 designs have become working prototypes for customers ranging from the California Institute of Technology and Rockwell International to MIT and Cree Research. In the last five years, Mr. Martin has expanded Halcyon's role as a service laboratory for package research and development into sensor development. He is a member of ISHM.